

III.A.23 Developing Low-Cr Fe-Ni-Based Alloys for Intermediate Temperature SOFC Interconnect Application

Objectives

- Develop a series of new Fe-Ni based alloys without Cr or with low Cr for intermediate temperature solid oxide fuel cell (SOFC) interconnect application.
- Demonstrate suitable oxidation resistance, oxide scale area specific resistance (ASR), and coefficient of thermal expansion (CTE) for these new alloys.
- Achieve low Cr evaporation rates for these alloys without surface coatings.

Accomplishments

- Over 200 alloys have been made by arc melting and drop casting, with various alloying elements added to narrow down some promising compositional ranges for further alloy development. Several strategies have been identified to improve oxidation resistance of low-Cr Fe-Ni-based alloys.
- A new low-Cr Fe-Ni-based alloy system has been identified. The oxidation resistance of the new low-Cr Fe-Ni-based alloy is much better than that of Fe-60Ni and comparable to that of Crofer22 APU. Furthermore, the new alloy also exhibits excellent resistance to cyclic oxidation.
- A low oxide scale ASR has been demonstrated for the new developmental low-Cr Fe-Ni-based alloy.
- The Cr evaporation rate of the new developmental alloy is much lower than that of Crofer22 APU under similar exposure conditions.

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Introduction

Solid oxide fuel cells (SOFCs) have attracted significant attention due to their benefits of environmentally benign power generation with fuel flexibility. However, the main hurdle thwarting the SOFC commercial introduction is lack of appropriate interconnect materials, which is of key importance for SOFC development. There has been recent interest in Cr₂O₃-forming alloys for SOFC interconnect applications because of the reduction in SOFC operating temperature. However, volatile Cr species generated from Cr₂O₃ in oxidizing atmospheres (on the cathode side) can cause severe degradation of the long-term performance of SOFCs because of cathode poisoning [1,2]. This SECA project has focused on the development of new low-Cr Fe-Ni-based interconnect alloys with low CTE and scale ASR, suitable oxidation resistance, and reduced Cr evaporation, which is expected to resolve the Cr poisoning issue for SOFC stacks.

Approach

Using alloy-design principles, we have developed a series of new low-Cr Fe-Ni-based alloys. These low-Cr Fe-Ni-based alloys with 6 wt.% Cr maximum are expected to develop a double-layer oxide scale consisting of a Cr-free, electrically-conductive (Fe,Ni)₃O₄ spinel outer layer to act as a surface seal for blocking Cr evaporation from the alloy surface atop a protective, electrically-conductive Cr₂O₃ inner layer. This project is being carried out as an interdisciplinary and collaborative endeavor with the involvement of two universities and one national laboratory.

So far, we have demonstrated the feasibility of thermally growing the double-layer oxide structure on the low-Cr Fe-Ni-based alloys. We have also characterized the isothermal and cyclic oxidation resistance, oxide scale ASR, and Cr evaporation rate of these low-Cr Fe-Ni-based alloys.

Results

Through a systematic alloy design effort, a low-Cr Fe-Ni-based alloy with drastically improved oxidation resistance has been developed. A preliminary evaluation of this alloy is summarized here. It should be noted that further alloy composition modifications are being pursued to optimize its overall performance.

Long-term isothermal oxidation testing at 800°C in air indicates that the oxidation resistance of the new low Cr Fe-Ni-based alloy was much higher than that of Fe-60Ni, and comparable to that of Crofer22 APU. As shown in Figure 1, after the first week, the weight gain of this low-Cr alloy increased slightly with time and its oxidation rate was similar to that of Crofer22 APU. The initially larger weight gain during the first week exposure for this alloy over Crofer22 APU is actually desirable, as it is due to the formation of a surface spinel outer layer. Compared to the binary Fe-60Ni alloy, an order of magnitude reduction in weight gain was achieved. The improved oxidation resistance of this new alloy resulted from the formation of a continuous, dense Cr_2O_3 inner layer between the Cr-free spinel layer and the substrate alloy as shown in Figure 2, which is the a cross-sectional view of this alloy after oxidation for 12 weeks at 800°C in air. The Cr_2O_3 inner layer acts as a barrier against

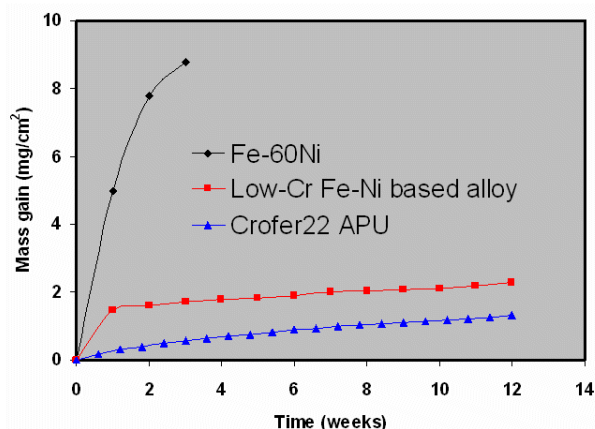


FIGURE 1. Isothermal Oxidation Kinetics of the Low-Cr Fe-Ni-Based Alloy in Air at 800°C

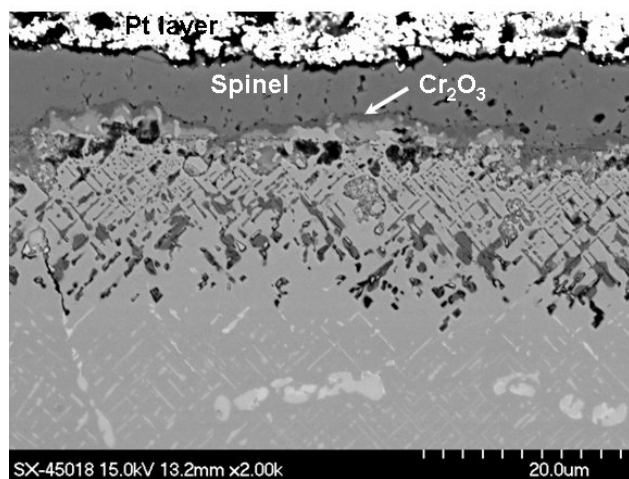


FIGURE 2. Cross-Section of the Low-Cr Fe-Ni-Based Alloy after 12-Week Oxidation in Air at 800°C

the oxidation process. From Figure 2, some internal oxidation was apparent and we are currently continuing our alloy design efforts to reduce/eliminate the internal oxidation problem.

The ASR of the oxide scale formed on this alloy after oxidation for 12 weeks is shown in Figure 3. The oxide scale ASR of this alloy was lower than that of Crofer22 APU after similar exposure. The low ASR of the oxide scale thermally grown on this alloy should be attributed to the high electrical conductivity of the spinel outer layer.

Cyclic oxidation tests were conducted to determine the adherence of the oxide scales formed on the new low-Cr Fe-Co-Ni-based alloy. Each cycle consisted of holding at 800°C in air for 25 hours followed by cooling to room temperature in air. No spallation was observed after 80 cycles with a cumulative exposure time of 2,000 hours, indicating good adhesion between the oxide scales and the alloy substrate. The mass gain of the low-Cr Fe-Ni-based alloy was significantly lower than that of the Fe-50Ni alloy, as shown in Figure 4. The adequate resistance to spallation resulted from the CTE match between the oxide scale and the substrate alloy.

Initial work was conducted by PNNL to evaluate the Cr volatility of the new low-Cr Fe-Co-Ni base alloy in moist air at 800°C for 500 hours with an air velocity of $1.1 \text{ cm}\cdot\text{s}^{-1}$. The Cr transport rate was $5.7 \times 10^{-12} \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ for this new alloy. For purpose of comparison, under identical conditions a value of $3.3 \times 10^{-11} \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ for Crofer22 APU was obtained. Therefore, the Cr volatility for the new low-Cr alloy was about a factor of almost six lower than that of Crofer22 APU. This is mainly due to the formation of the Cr-free spinel outer layer that blocks the Cr evaporation from the chromia inner layer.

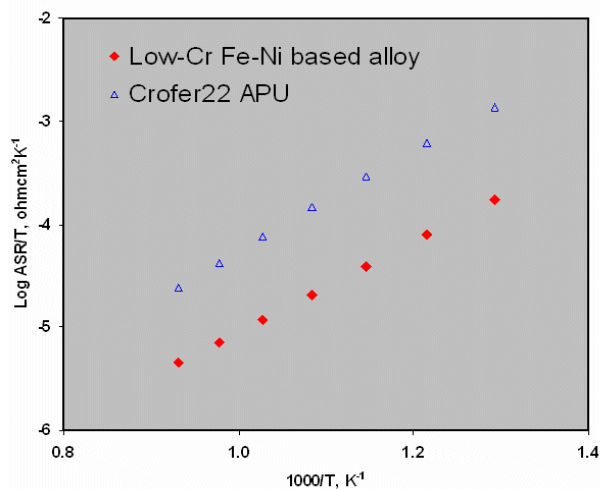


FIGURE 3. Comparison in Scale ASR of the Low-Cr Fe-Ni-Based Alloy with Crofer22 APU after 12-Week Oxidation in Air at 800°C

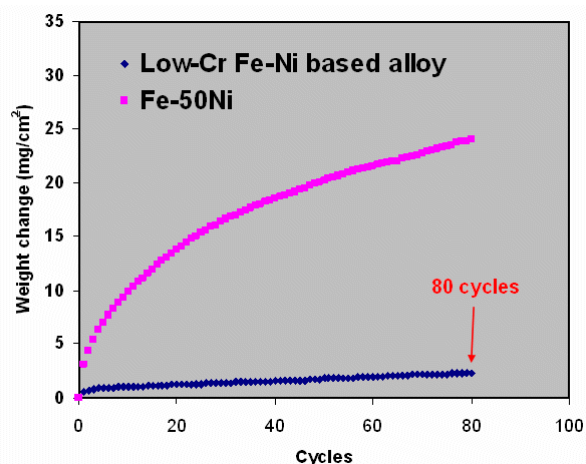


FIGURE 4. Cyclic Oxidation Kinetics of the Low-Cr Fe-Ni-Based Alloy and the Fe-50Ni Alloy in Air at 800°C

Conclusions and Future Directions

The formation of an electrically conductive, Cr-free spinel outer layer atop a protective, electrically conductive oxide inner layer on the metallic interconnects is highly desirable to mitigate the Cr poisoning problem in the SOFC stack. Our preliminary results indicate that a double-layer oxide structure with an electrically conductive, Cr-free spinel outer layer and a protective Cr_2O_3 inner layer could be thermally grown on a new low-Cr Fe-Ni-based alloy with drastically improved oxidation resistance, low scale ASR, and CTE match with other cell components. While additional alloy design and production scale-up is clearly needed, this study has demonstrated that it is feasible to develop a low-Cr Fe-Ni alloy with balanced properties for SOFC interconnect application. This alloy system contains significantly less Ni than Ni-based superalloys and much less Cr than ferritic steels, while their manufacturability is similar to ferritic steels. Therefore, the cost-effective new alloy interconnects will be very attractive for reducing the overall cost and improving the durability of SOFC stacks.

Future directions for this project are listed below:

- **Further optimization of the composition range of the new Fe-Ni base alloys.** The composition range of these alloys will be further narrowed down with special attention paid to reduce/eliminate the internal oxidation zone between the Cr_2O_3 inner layer and the alloy substrate after thermal exposure in air.
- **Characterization of oxidation/corrosion behavior in both single and dual-atmosphere condition.** The oxidation behavior of the low-Cr Fe-Ni-based

alloys will be studied at 700-900°C in both air (cathode environment) and $\text{Ar}+4\%\text{H}_2+3\%\text{H}_2\text{O}$ which corresponds to the anode environment. In addition, selected alloy coupons will also be exposed to dual atmospheres (one side air and the other side $\text{H}_2+3\%\text{H}_2\text{O}$) at 800°C. The oxide scale features formed after the dual-atmosphere exposure will be compared to those formed in single atmosphere alone.

- **Compatibility and in-cell performance evaluation.** The interaction and compatibility of the new interconnect alloys with the contact and cathode materials will be conducted using screen-printed interconnect/contact/cathode couples. After thermal exposure of the couple, ASR measurement will be conducted to get the overall resistance of the couple and possible formation of insulating phase(s) at the interface and Cr migration into the cathode will be identified. The effect of the new interconnect alloys on the cell performance will be conducted with a SOFC test stand. The cell performance with different interconnect alloys will be compared and the Cr volatility of the new Fe-Ni alloys will be assessed.

Special Recognitions & Awards/Patents Issued

1. An invention disclosure on the new low-Cr Fe-Ni alloys has been completed.

FY 2006 Publications/Presentations

1. "Oxidation Behavior and Electrical Properties of NiO- and Cr_2O_3 -Forming Alloys for Solid Oxide Fuel Cell Interconnects", *Oxidation of Metal*, in press, 2006.
2. "Evaluation of Several Low Thermal Expansion Fe-Co-Ni Alloys as Interconnect for Reduced-Temperature Solid Oxide Fuel Cell", *International Journal of Hydrogen Energy*, submitted, 2006.
3. "Evaluation of Several Fe-Ni Alloys for SOFC Interconnect Application", Poster Presentation, Gordon Research Conference on High-Temperature Corrosion, New London, NH, July 24-27, 2005.
4. "Tailoring Fe-Ni Based Alloys for Intermediate Temperature SOFC Interconnect Application", Presentation, SECA Core Technology Program Peer Review Meeting, Denver, CO, October 25-26, 2005.
5. "Evaluation of Fe-Ni Alloys for Reduced-Temperature SOFC Interconnect Application", Invited Presentation, Symposium on Materials in Clean Power Systems: Applications, Corrosion, and Protection, TMS Annual Meeting & Exhibition, San Antonio, TX, 12-16 March 2006.

References

1. Gindorf, C., Singheiser, L. & Hilpert, K. Chromium Vaporization from Fe,Cr Base Alloys Used as Interconnect in Fuel Cells. *Steel Research* 72 (11-12), 528-533 (2001).
2. Matsuzaki, Y. & Yasuda, I. Electrochemical Properties of a SOFC Cathode in Contact with a Chromium-Containing Alloy Separator. *Solid State Ionics* 132, 271-278 (2000).